Comparison of the Properties of Ni–Mn Hydroxides/Oxides with Ni–Mn Phosphates for the Purpose of Hybrid Supercapacitors

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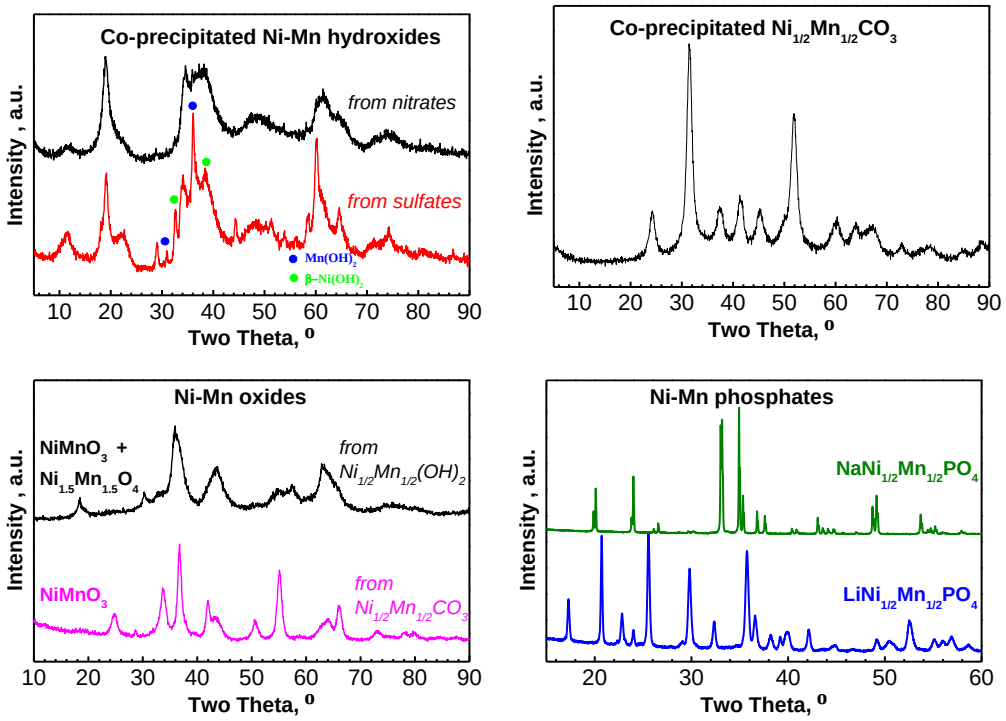

Figure S1. XRD patterns of Ni-Mn based mixed hydroxides, carbonate, oxides and phosphates

The XRD patterns of all samples are indexed taking into account the ICSD database.

XRD pattern of the precipitated Ni-Mn carbonate is indexed in the calcite-type structure with lattice parameters of a = 4.724 Å, c = 15.52 Å, V = 300.0 Å^3. These values are intermediate between those for $NiCO_3$ (a = 4.6117 Å, c = 14.735 Å, V = 271.4 Å^3 [1]) and $MnCO_3$ (a = 4.772 Å, c = 15.637 Å, V = 308.4 Å^3, [2]). From the chemical analysis the Ni/Mn ratio is 0.96, so that the composition is $Ni_{1/2}Mn_{1/2}CO_3$.

The precipitation with nitrate salts yields a single $Ni_{1/2}Mn_{1/2}(OH)_2$ phase, that is isostructural to well-known β-$Ni(OH)_2$ (ICSD 28101), while a mixture between α- and β-type $Ni_xMn_{1-x}(OH)_2$, as well as individual $Mn(OH)_2$ (ICSD 23591) and β-$Ni(OH)_2$, is obtained when nickel and manganese sulfate salts are used (Fig. S1).

The oxide $NiMnO_3$ prepared after the thermal decomposition of $Ni_{1/2}Mn_{1/2}CO_3$ is characterized by an ilmenite-type of structure (ICSD 31853), while a mixture between ilmenite phase $NiMnO_3$ and a spinel phase $Ni_{1.5}Mn_{1.5}O_4$ is formed after decomposition of single β-$Ni_{1/2}Mn_{1/2}(OH)_2$ phase. The XRD pattern of the spinel phase is very similar to that of cubic $NiMn_2O_4$ (ICSD 185294).

XRD data evidence for the formation of single phase of $LiNi_{1/2}Mn_{1/2}PO_4$ and $NaNi_{1/2}Mn_{1/2}PO_4$. $LiNi_{1/2}Mn_{1/2}PO_4$ adopts an olivine-type structure (SG *Pnma*) that is characteristic for the end members, $LiMnPO_4$ and $LiNiPO_4$, with lattice parameters: a = 10.2469(6) Å; b = 5.9858(3) Å; c = 4.7152(3)Å; V = 289.05(3) $Å^3$. In contrast, sodium compound $NaNi_{1/2}Mn_{1/2}PO_4$ is characterized by a maricite type structure (also SG *Pnma*) with the following lattice parameters: a = 8.9233(1) Å; b = 6.8207(1) Å; c = 5.0744(1)Å; V = 308.852(7) $Å^3$. It is important that for both mixed phosphates the unit-cell volume has an intermediate value between these for the corresponding end members, Li(Na)$MnPO_4$ and Li(Na)$NiPO_4$, which confirms the formation of mixed crystals [3-6]. The olivine- and maricite type structures are closely related each other: they have the same PO_4 framework, but with a reverse distribution of M^+ and M^{2+} ions over the two octahedral sites (4*a* and 4*c* sites). In the olivine structure Ni/Mn ions are randomly distributed on the 4*c* octahedral sites, while in the maricite structure – on the 4*a* crystallographic sites. To the best of our knowledge, we report the first crystallographic data for these mixed Ni-Mn based phosphate compositions.

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